SELECTIVE GROWTH METHOD FOR COMPOUND SEMICONDUCTOR

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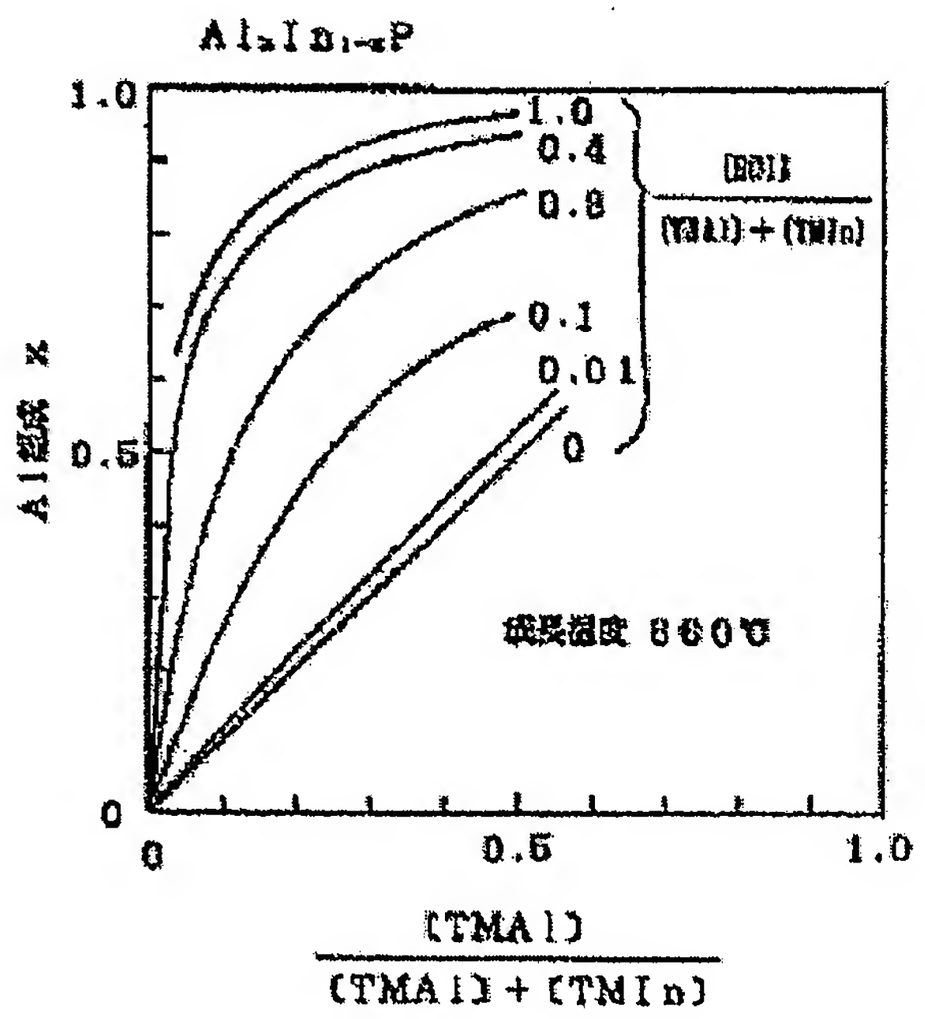
Abstract of **JP7297134**

PURPOSE:To provide a method for growing a compound semiconductor composition selectively with high uniformity within a 2 inch wafer and high reproducibility of composition control. CONSTITUTION:In the method for growing a III-V compound containing at least Al and In selectively by an MOVPE method added with HCL, the ratio of supply quantity of HCl to the total supply quantity of group III organic metal material is set in the range of 0.01-0.3. This method prevent growing of an Al rich layer while sustaining the selectivity and facilitates control of the composition.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the method of carrying out selection crystal growth of the group III-V semiconducter who contained aluminum and In at least on the semiconductor substrate which covered surface [a part of] with the insulator layer by the metal-organic chemical vapor deposition (it abbreviates to MOVPE method hereafter) of HCl addition.
[0002]
[Description of the Prior Art]The selective growth art of covering a part of semiconductor surface with insulator layers, such as silicon nitride and silicon oxide, and growing up a semiconducting crystal only into the portion which is not covered is very effective art on production of optical devices, such as a laser diode, and a light emitting device and the optical integrated element which accumulates an electric circuit on the same board. In the case of the semiconductor which does not contain aluminum, such as GaAs and InP, crystal growth can be selectively carried out only to the substrate face which has not been easily covered with an insulator layer with the usual MOVPE method. For example, electronics Letters (Electronics Letters)Vol.28(1992)p153. On the other hand, since the semiconductor (AlAs and aluminum$_Z$Ga$_{1-Z}$ As of high Al composition) having contained aluminum is deficient in aluminum growth kind in volatility, selective growth by the usual MOVPE method is made very difficult. Therefore, selective growth is realized by adding the substance which contains Cl(s), such as HCl and $AsCl_3$, during growth, and forming volatile high chloridation aluminum. Conventionally, in order that the selective growth of AlAs or aluminum$_Z$Ga$_{1-Z}$ As of high Al composition may obtain sufficient selectivity, the ratio ([HCl amount of supply] /[III fellows amount of supply]) of the HCl amount of supply to the total amount of supply of an III fellows organic metal raw material is performed in 0.4-1.0. .In aluminum$_Z$Ga$_{1-Z}$ As, that Al composition differs by the case where it does not add with the case where HCl is added as shown in drawing 4. Journal OBU Crystal Glaus (Journal of Crystal Growth) Vol.124. (1992) It is reported to p235-242. Drawing 4 is 4.2K photoluminescence spectrum of aluminum(growing temperature of 800 **) $_Z$Ga$_{1-Z}$ As grown-up by the case where it adds with the case where HCl is not added. It turns out that a luminous wavelength will carry out short wavelength formation if HCl is added, and Al composition is increasing.
[0003]
[Problem(s) to be Solved by the Invention]aluminum$_Z$Ga$_{1-Z}$ As is so small that it can disregard the Al composition dependency of a grating constant, and does not need to take into consideration the stacking fault which poses a device manufacturing top problem. Therefore, even if the presentation of aluminum$_Z$Ga$_{1-Z}$ As which carried out selective growth by HCl addition changed, the problem in particular was not produced.
[0004]The group III-V semiconducter (for example, aluminum$_X$In$_{1-X}$P) who contains aluminum and In at least on the other hand has the large Al composition dependency of a grating constant. Therefore, if HCl addition is carried out and a grating constant shifts, if distortion goes into a crystal and the limit of stress is exceeded, a defect will be introduced, and if the case where it applies to a device is assumed, operation of a device and its operational reliability will be worsened.
[0005]Although there is no example of a report which added HCl and carried out selective growth in the group III-V semiconducter containing aluminum and In in the

former, naturally an above-mentioned problem is expected. What is necessary will be to grasp the quantity from which a lattice shifts as that management, and just to amend the organic raw metarial amount of supply of aluminum and In at the time of crystal growth at this time. However, AlInP in which lattice matching is possible to a GaAs substrate, AlGaInP, and AlInAs in which lattice matching is possible to an InP substrate are received, When selective growth was carried out with reference to the above-mentioned example of a report about AlGaAs, the problem that it was the whole 2-inch wafer, and the selective growth which carried out lattice matching to the substrate could not be obtained with sufficient reproducibility for every trial time was encountered.

[0006]The purpose of this invention removes an above-mentioned problem, and when carrying out selective growth of the III-V compound semiconductor which contains aluminum and In at least with the MOVPE method of HCl addition, there is in providing the method of obtaining easily the selective growth crystal layer which reproducibility improved lattice matching to the substrate of the large area.

[0007]

[Means for Solving the Problem]In a method of carrying out crystal growth of the group III-V semiconducter who this invention supplies HCl, an III fellows organic metal raw material, and V group material on a semiconductor substrate which covered surface [a part of] with an insulator layer, and contains aluminum and In at least, A ratio ([HCl amount of supply] /[III fellows amount of supply]) of the HCl amount of supply to the total amount of supply of said III fellows organic metal raw material grows up to be only a substrate face which is not covered with an insulator layer in said group III-V semiconducter as 0.3 or less [0.01 or more] selectively.

[0008]

[Function]An operation of the crystal growth method of this invention is explained in detail. When drawing 1 performs selective growth by HCl addition to GaAs in the aluminum$_X$In$_{1-X}$P mix crystal in which lattice matching is possible, The [HCl amount of supply] The value of / [III fellows amount of supply] to 0-1.0. The relation between the Al composition (aluminum solid phase ratio) of the aluminum$_X$In$_{1-X}$P growth film at the time of making it change, and the ratio (the [TMAl amount of supply] / [III fellows amount-of-supply]:aluminum gaseous phase ratio) of the trimethylaluminum (TMAl) amount of supply to the total amount of supply of an III fellows organic metal raw material. It is shown. The growing temperature of the aluminum$_X$In$_{1-X}$P film at this time is 660 **. When [HCl amount-of-supply]/[III fellows amount of supply] is 0 so that clearly from this figure (i.e., when not adding HCl), Al composition increases linearly in proportion to aluminum gaseous phase ratio, and is understood that control of a presentation is easy. However, if [HCl amount-of-supply]/[III fellows amount of supply] is made to increase, a graph will curve greatly and will become overaluminum. Although the composition ratio x (solid phase ratio) carries out lattice matching of the aluminum$_X$In$_{1-X}$P to GaAs by 0.5, in the neighborhood, a solid phase ratio changes sensitively to a gaseous phase ratio for an above-mentioned curve.

[0009]In 0.4-1.0, wandering of aluminum gaseous phase ratio will be 15 or more times, and [HCl amount-of-supply]/[III fellows amount of supply] currently indicated as conditions for obtaining selectivity conventionally sufficient with the selective growth of AlGaAs appears in a solid phase ratio. Considering putting the accuracy of a massflow controller and the organic raw metarial (trimethylindium) of In which control the amount of actual condition feeding on carrier gas by sublimation from a solid, and supplying them, it is assumed that there is 1% of wandering in control of aluminum gaseous phase ratio. 1% of this wandering corresponds to 15% of

wandering in a solid phase ratio. If a presentation shifts from lattice matching conditions no less than 15%, it is difficult to obtain a growth phase of 1 micrometers or more with few lattice defects, and it is not a level which can produce a device. Conversely, if it says, it will be thought that a gaseous phase ratio must be controlled by very high accuracy.

[0010]Next, control of aluminum gaseous phase ratio assumes that it has controlled to 0.1%. Even in this case, generally it is thought appropriate to conclude that the usual MOVPE apparatus has about 1% of composition distribution with a 2-inch wafer with the shape of a coil, etc. It must be considered that it becomes 15 or more times and this distribution also appears. These are not having become a problem in AlGaAs which is not depended on a presentation but carries out lattice matching to a GaAs substrate mostly.

It is the reason which the diversion from AlGaAs was not able to perform to AlInP. However, if the value of [HCl amount-of-supply]/[III fellows amount of supply] uses 0.3 or less, an above-mentioned curve is also comparatively small and composition control is easy for it. The [HCl amount of supply] When the value of / [III fellows amount of supply] is 0.3, wandering of aluminum gaseous phase ratio can be made into a solid phase ratio, and can be stopped within 2.5 times as many wandering, the field of a 2-inch wafer -- internal division -- growth phases of 1 micrometers or more with few lattice defects also including cloth can be obtained easily, and application to a device is attained. Therefore, when the controllability of a presentation of aluminum$_X$In$_{1-X}$P is considered, a practical AlInP selective growth film can be obtained only after being able to make [HCl amount-of-supply]/[III fellows amount of supply] or less into 0.3.

[0011]The [HCl amount of supply] Naturally the minimum of / [III fellows amount of supply] is decided with selectivity. Drawing 2 shows the density of the AlInP polycrystal which deposited on the nitriding silicon mask with a 5-micrometer length [in width] of 500 micrometers, and the relation of [HCl amount-of-supply]/[III fellows amount of supply] in the selective growth of HCl addition aluminum$_X$In$_{1-X}$P. The size of the mask assumed the stripe of laser. When the number of average polycrystal is one or less, a laser stripe can be judged that formation is possible. In aluminum$_X$In$_{1-X}$P growth, by supplying HCl slightly, the density of polycrystal falls rapidly and selectivity improves. The [HCl amount of supply] from this result It turns out that selectivity is fully obtained for / [III fellows amount of supply] or more by 0.01.

[0012]A selective growth layer applicable to a device will not be able to be obtained without considering selectivity for [HCl amount-of-supply]/[III fellows amount of supply] with the selective growth of aluminum$_X$In$_{1-X}$P from the above result, considering the controllability of a presentation or more by 0.01, and carrying out or less by 0.3.

[0013]

[Example]The example of AlInP by this invention and AlInAs selective growth is indicated below.

[0014]Selective growth of AlInP and AlInAs was performed with the MOVPE method of decompression (70torr). Using TMAl and trimethylindium (TMIn) as a group III material, the amount of supply of TMIn was fixed by 1.92×10^{-5}mol/min, and Al composition was changed by changing the amount of supply of TMAl with 0.03 - 1.80×10^{-5}mol/min. In 10% of hydrogen dilution, as a V group material, HCl used HCl for the 10% arsine (AsH_3) of 100% phosphoretted hydrogen (PH_3) and H_2 dilution. The flows of PH_3 and AsH_3 are 150sccm and 50sccm, respectively. The

amount of supply of HCl was changed so that the ratio ([HCl amount of supply] /[III fellows amount of supply]) of the HCl amount of supply to that total of a group III material might be set to 0.01-1.0. The total flow in a coil is 14.5 l. / min, using H_2 in the carrier gas of a raw material. A substrate is GaAs(001) 2 degreeoff to. Silicon nitride with a thickness of 300 nm made to deposit by the plasma chemistry depositing method was used for the mask using [110]. The thickness of the growth phase could be 1 micrometer. The presentation of the growth phase was searched for from the component analysis (EPMA) by the characteristic X ray of an X diffraction peak and aluminum.

[0015]Drawing 1 graph-izes relation between Al composition ratio x (solid phase ratio) and aluminum gaseous phase ratio to [HCl amount-of-supply]/[III fellows amount of supply]. These contents were described in detail on the occasion of explanation of "OPERATION."

[0016]

[Table 1]

AlxIn1-xP

[HCl供給量]/[III族供給量] = 0.1		[HCl供給量]/[III族供給量] = 0.4	
[TMAl]/[III族]	Al組成X	[TMAl]/[III族]	Al組成X
0.23	0.486	0.02	0.372
0.24	0.503	0.03	0.501
0.25	0.508	0.04	0.575
0.24	0.503	0.03	0.521
0.24	0.501	0.03	0.493
0.24	0.505	0.03	0.519

[0017]Table 1 is the detailed result of [HCl amount-of-supply]/[III fellows amount of supply] trying the growth of $aluminum_{0.5}In_{0.5}P$ which carries out lattice matching to a GaAs (001) side with the value of a report this invention which is 0.1, and conventionally which is 0.4. In order to examine the controllability of a presentation, change of the presentation at the time of changing slightly the ratio (aluminum gaseous phase ratio) of the TMAl amount of supply to the total amount of supply of an III fellows organic metal raw material was considered. The stability of composition control when the same gaseous phase ratio is grown up two or more times was also examined. When [HCl amount-of-supply]/[III fellows amount of supply] is 0.1 so that clearly from Table 1, even if it changes aluminum gaseous phase ratio from 0.23 to 0.25, change of Al composition is as small as 0.486 to 0.508. Change of Al composition is small also from the result aluminum gaseous phase ratio grew up to be repeatedly by 0.24.

[0018]On the other hand, when [HCl amount-of-supply]/[III fellows amount of supply] is 0.4, if aluminum gaseous phase ratio is changed from 0.02 to 0.04, Al composition will change a lot from 0.372 to 0.575. In this case, it turns out that the amount of supply of TMAl must be controlled strictly. The Al composition for every growth time in aluminum gaseous phase ratio 0.03 also has a large change, and there

is a problem in reproducibility. Except the center section of a 2-inch wafer, the morphology of the shape of crosshatch considered to originate in distortion of a lattice is observed. Therefore, when performing lattice matching which is needed on device manufacturing, [HCl amount-of-supply]/[III fellows amount of supply] is difficult for the composition control of AlInP in 0.4.

[0019]When the growing method of this invention performs selective growth of aluminum$_X$In$_{1-X}$P from the above example, it turns out that it excels in composition control.

[0020]Although this example described AlInP, the composition ratio of aluminum and Ga is in the almost same tendency also to AlGaInP of 0.7 to 0.3 or more high Al composition, and this invention can be applied also to AlGaInP of high Al composition. It is thought that AlGaInP and AlInP can apply this invention in the range with a temperature of 630 to 720 ** by which crystal growth is generally carried out.

[0021]Drawing 3, The relation between the Al composition of aluminum$_X$In$_{1-X}$ As grown-up with HCl addition MOVPE method and the ratio (the [TMAl amount of supply] / [III fellows amount-of-supply]:aluminum gaseous phase ratio) of the trimethylaluminum (TMAl) amount of supply to the total amount of supply of an III fellows organic metal raw material is shown. Growing temperature is 700 **. Although there is a difference in some compared with the result of AlInP shown by drawing 1, the almost same tendency is shown. Therefore, it is thought like the time of AlInP by making [HCl amount-of-supply]/[III fellows amount of supply] or less into 0.3 that a practical selective growth layer can be obtained. About this, it can guess as follows from the standard enthalpy of formation (binding energy) of each group III-V semiconducter who showed in Table 2. The difference of the binding energy of AlP and InP is as large as 21.3 kcal/mol, and if HCl is added, a presentation gap will take place easily. Therefore, if [HCl amount-of-supply]/[III fellows amount of supply] is controlled or less to 0.3, the compound below a 21.3 kcal/mol difference will be considered that composition control is possible. Since the binding energy difference of AlAs and InAs is in the range by 15.5 kcal/mol in AlInAs, it is thought that this invention is applicable.

[0022]Although this example described the case of AlInP and AlInAs, if the energy difference between each compound is calculated from the value of the binding energy shown in Table 2, it is possible to obtain a practical selective growth layer by this invention not only about AlGaInP which touched also in advance but about AlInAsP -- it thinks.

[0023]

[Table 2]

(単位：kcal／mol)

AlN	-76.1	GaN	-26.2	InN	-33.0
AlP	-39.3	GaP	-29.2	InP	-18.0
AlAs	-29.3	GaAs	-19.5	InAs	-13.8
AlSb	-12.0	GaSb	-10.0	InSb	-7.44

[0024]

[Effect of the Invention]As mentioned above, in the selective growth of the group III-V semiconducter by this invention, [HCl amount-of-supply]/[III fellows amount of supply] is carried out more than 0.01V, selectivity is raised, and the controllability of a presentation is improved by making [HCl amount-of-supply]/[III fellows amount of

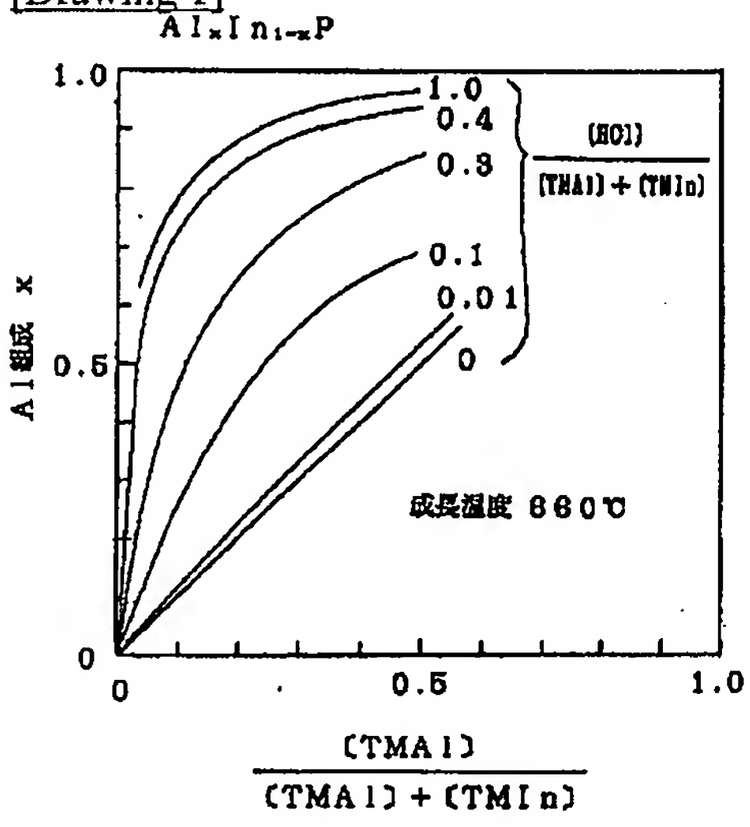
supply] or less into 0.3. It has the advantage that composition control is good and can carry out selective growth of the result on the substrate of a large area.

CLAIMS

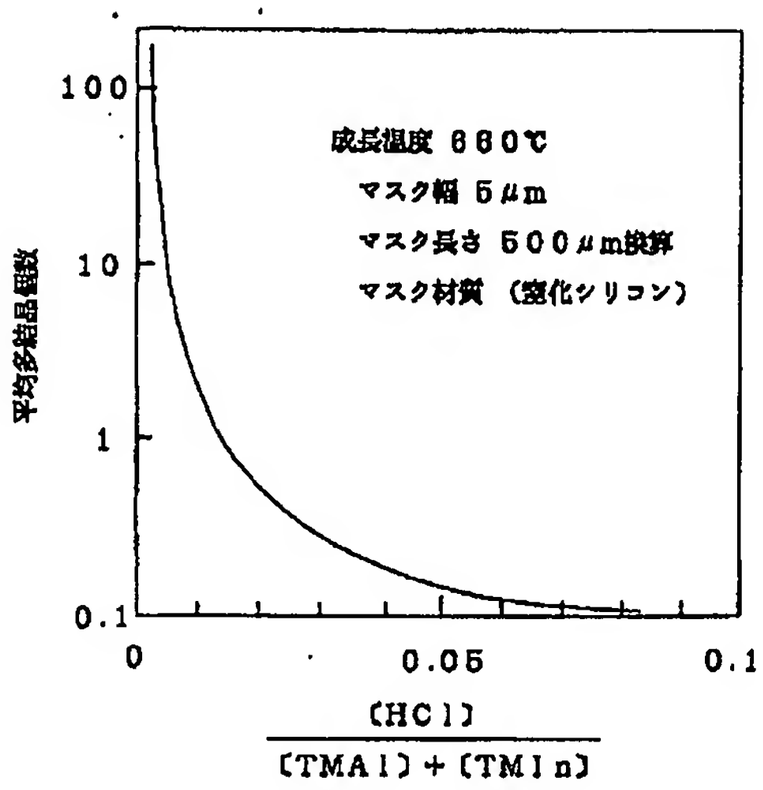
[Claim(s)]
[Claim 1]In a method of carrying out crystal growth of the group III-V semiconducter who supplies HCl, an III fellows organic metal raw material, and V group material on a semiconductor substrate which covered surface [a part of] with an insulator layer, and contains aluminum and In at least, A selective growth method of a compound semiconductor making a ratio ([HCl amount of supply] /[III fellows amount of supply]) of the HCl amount of supply to the total amount of supply of said III fellows organic metal raw material or less [0.01 or more] into 0.3, and making it grow up to be only a substrate face which is not covered with said insulator layer selectively.

DRAWINGS

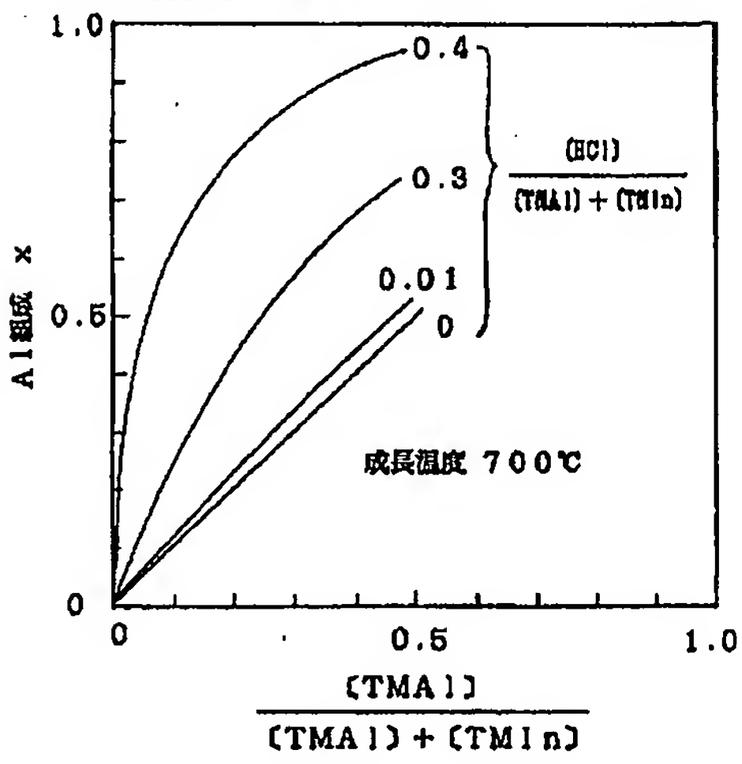
[Drawing 1]



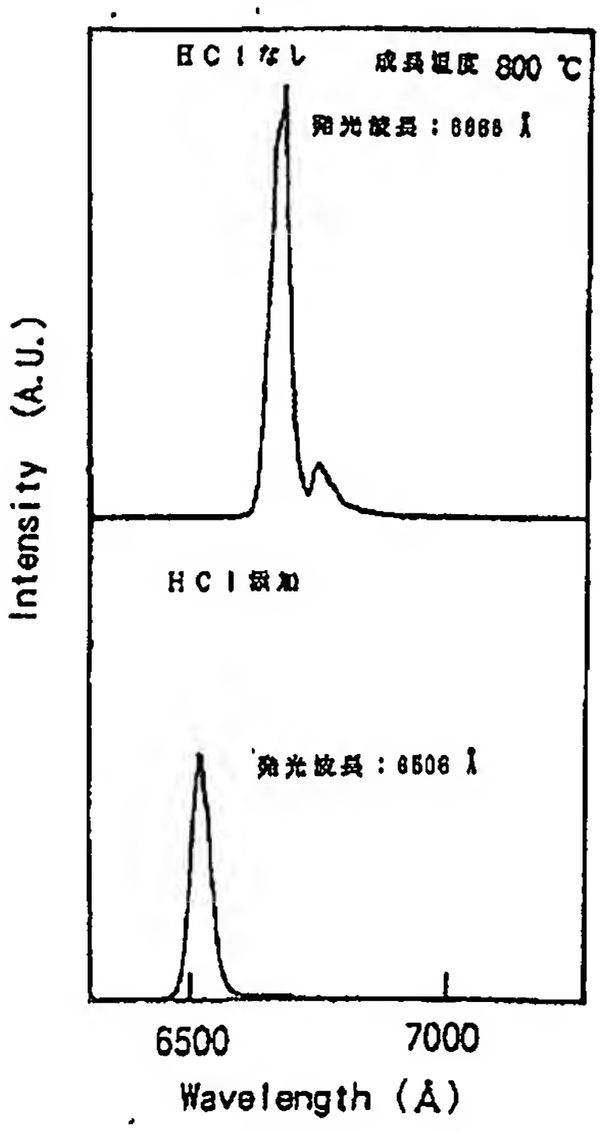
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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(54)【発明の名称】　化合物半導体の選択成長方法

(57)【特許請求の範囲】

【請求項１】表面の一部を絶縁膜で覆った半導体基板上にＨＣｌとＩＩＩ族有機金属原料とＶ族原料を供給して、少なくともＡｌとＩｎを含むＩＩＩ－Ｖ族化合物半導体を結晶成長する方法において、前記ＩＩＩ族有機金属原料の全供給量に対するＨＣｌ供給量の比率（［ＨＣｌ供給量］／［ＩＩＩ族供給量］）を０．０１以上０．３以下として、前記絶縁膜で覆われていない基板表面だけに選択的に成長させることを特徴とする化合物半導体の選択成長方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明はＨＣｌ添加の有機金属気相成長法（以下、ＭＯＶＰＥ法と略す）により、少なくともＡｌとＩｎを含んだＩＩＩ－Ｖ族化合物半導体を、表面の一部を絶縁膜で覆った半導体基板上に選択結晶成長させる方法に関するものである。

【０００２】

【従来の技術】半導体表面の一部を窒化シリコンや酸化シリコンなどの絶縁膜で覆い、覆われていない部分にのみ半導体結晶を成長させる選択成長技術は、レーザダイオードなどの光デバイスや、発光素子と電気回路を同一基板上に集積する光集積素子の作製上非常に有効な技術である。ＧａＡｓやＩｎＰ等のＡｌを含まない半導体の場合、通常のＭＯＶＰＥ法で容易に絶縁膜で覆っていない基板表面のみに選択的に結晶成長できる。例えば、エレクトロニクス・レターズ（Ｅｌｅｃｔｒｏｎｉｃｓ Ｌｅｔｔｅｒｓ）Ｖｏｌ．２８（１９９２）ｐ１５３。一方、Ａｌを含んだ半導体（ＡｌＡｓや高Ａｌ組成の$Al_zGa_{1-z}As$）は、Ａｌ成長種が揮発性に乏しいた